

IAP20 Rec'd PCT/PTO 11 JAN 2006

Method for reducing the formaldehyde and cyanide
contents in solutions of sarcosine salts

Description

5

The present invention relates to a method for reducing the formaldehyde and cyanide contents in technically produced solutions of salts of sarcosine (sarcosinates).

10

Sarcosinates are at present mainly prepared according to the "Strecker synthesis" from the starting compounds formaldehyde, hydrocyanic acid and methylamine, the sarcosine nitrile formed as intermediate being
15 subjected, in a final stage of the method, to hydrolysis using an alkaline solution (cf., e.g., DE-PS 25 03 582).

20

Depending on the stoichiometric ratios chosen for the starting compounds used, residual amounts of individual educts at the same time remain in the resulting sarcosinate solution. While in this connection excess methylamine, as well as the amounts of ammonia liberated in the hydrolysis, can be completely removed
25 by distillation according to the state of the art, the starting compounds cyanide or formaldehyde remain to a large extent in the product, in the case of hydrocyanic acid or formaldehyde having been used in non-equimolar amounts under the processing conditions.

30

In order to be able to reduce the two last named starting compounds in the product to less than ppm ranges, both have to be used in exactly the same stoichiometry, which, however, is extremely difficult
35 from a processing viewpoint and is consequently also cost intensive.

Surprisingly, cyanide and also formaldehyde have proven

to be very stable in a strongly alkaline sodium sarcosinate solution, these compounds not being satisfactorily decomposed even under boiling conditions maintained for several hours.

5

Because of its toxicity, cyanide is frequently used in deficit in such amounts that formaldehyde remains in the resulting sodium sarcosinate solution and, in this connection, a residual content is accepted which, in industrial samples, can in some cases be much greater than 1 000 ppm. However, with minor variations in the amounts metered in, batches with high residual contents of cyanide can also be obtained.

15 The product sodium sarcosinate is mainly used for the preparation of detergents in the detergent field. It is certainly also already currently of great importance, and this importance will also carry on increasing, as raw material for the preparation of creatine, which for its part is used as food supplement (cf., for example, EP-A 751 122).

25 The last named use requires a grade in which the formaldehyde contaminants are far below the abovementioned values. In addition, the content of cyanide should be in the range of < 10 ppm.

30 From the disadvantages of the state of the art as outlined, in view of the required and actual residual amounts of starting compounds, the present invention has had the object of providing a simple method for reducing the formaldehyde and/or cyanide contents in technically produced sarcosinate-comprising solutions. In this connection, grades of the sarcosinate solutions thus obtained which are suitable for creatine production should in particular be achieved. In addition, the method should also make possible the preparation of other commercial sarcosinate solutions.

This object was achieved with a method in which a sarcosinate starting solution is subjected to a thermal treatment, in which the starting solution

5 a1) at an approximately equimolar ratio of formaldehyde and cyanide components of 1:0.9 to 1.1, is adjusted to temperatures between 20 and 120°C,

or

10 a2) at a non-equimolar ratio of formaldehyde and cyanide components, is heated to temperatures between 120 and 200°C,

and

b) is finally cooled down.

15 Surprisingly, it has been shown that, under the processing conditions a1) and/or a2) chosen, the decomposition of the cyanide or formaldehyde contaminants clearly increases but, simultaneously, the actual product of value, the sarcosinate, remains stable in the solution obtained. In this connection, it

20 was in particular not foreseeable that, to accelerate the decomposition, in particular at reduced processing temperatures, sodium cyanide can be added in the presence of formaldehyde residues in the product solution in an equivalent stoichiometry in comparison

25 with the formaldehyde, and vice versa. In this connection, a processing temperature simply lying slightly above normal room temperature is sufficient. The decomposition of the contaminants can in this connection be precisely monitored analytically.

30

In addition, it has been found that both cyanide and formaldehyde residues are quickly decomposed if the aqueous sarcosinate solution is heated to temperatures > 120°C. This was in particular not to be expected for

35 that since, as already explained, an astonishing stability in sarcosinate solutions is well known with regard to cyanide and formaldehyde. The course of the known Cannizzaro reaction, even under boiling conditions of ca. 105 to 110°C, does not take place

fast enough to satisfactorily remove formaldehyde. Usually, the thermally induced hydrolysis of cyanide under alkaline conditions, such as that, for example, well known from the decontamination of waste water, also does not occur sufficiently quickly in the sarcosinate solution.

The advantages of this new method could not to this extent be anticipated.

10

As already mentioned, the method according to the invention is mainly directed towards the purification of solutions comprising sodium sarcosinate. However, other kinds of sarcosinate solutions can also be purified, e.g. other alkali metal sarcosinate solutions or alkaline earth metal sarcosinate solutions. In the context of the present invention, the duration of the heat treatment is preferably 1 to 300 minute(s) and particularly preferably 40 to 60 minutes.

20

It has likewise been shown to be advantageous if, in the case of the processing stage a1), the starting solution is adjusted, by addition of calculated amounts of formaldehyde or cyanide, to an approximately equimolar ratio of these two compounds. After adjusting this approximately equimolar ratio, extensive and fast decomposition of the contaminants occurs.

In this connection, it can likewise be advantageous if, in the processing stage a1), the calculated amount of formaldehyde or cyanide is added in the form of an aqueous solution, which is likewise part of the present invention.

35 With regard to the processing temperature, temperatures of the starting solution between 60 and 110°C and particularly preferably between 90 and 105°C have been shown to be particularly suitable for the processing stage a1).

For the alternative first processing stage a2), a temperature range between 140 and 170°C is to be regarded as particularly preferred, it being possible
5 for the present method preferably to be carried out under pressure condition circumstances ≤ 10 bar.

In accordance with the problem, the objective, inter alia, was to prepare sarcosinate solutions suitable for
10 the manufacture of creatine. For this reason, inter alia, the present invention also comprises an alternative form of the method in which the formaldehyde content is reduced to values < 50 ppm and the cyanide content is reduced to values < 10 ppm. The
15 method is carried out particularly successfully in a 40% by weight sarcosinate solution.

Since the starting solutions can, in addition to formaldehyde and cyanide, also still comprise other
20 educts or byproducts, it is possible, before or during the actual thermal treatment, to separate educts, such as, e.g., methylamine, and/or byproducts, such as, e.g., ammonia, from the starting solution by distillation.

25 The preferred embodiments of the present method can be described as follows:

A commercial sodium sarcosinate solution obtained by
30 the Strecker synthesis, which comprises formaldehyde or cyanide residues, is heated under pressure conditions to a temperature of 120 to 200°C. This can be carried out batchwise in a reactor or continuously in a residence time vessel, which should both be
35 manufactured from alkali-resistant materials. After a residence time of ideally 40 to 60 minutes, the solution is cooled down.

Alternatively, with analytically determined contents of

contamination with formaldehyde or sodium cyanide, in each case the other of the two compounds can be added in such an amount that an approximately equimolar ratio of 1:0.9 - 1.1 results. Subsequently, the solution is
5 heated to 60 to 110°C and, after a residence time of ideally 40 to 60 minutes, is cooled down.

Even if starting concentrations of formaldehyde or cyanide of > 500 ppm were present, residual contents of
10 < 50 ppm of formaldehyde and < 10 ppm of cyanide are obtained with this method.

In case it should be intended to adjust the concentration of the solution to a preset value, the
15 thermal treatment stage for the sarcosinate solution can also be carried out while concentrating.

All in all, using the claimed method, formaldehyde and cyanide contents in technically produced sarcosinate-
20 comprising solutions are economically reduced to an extent which makes the products obtained suitable in particular also as raw material for the manufacture of creatine.

25 The following examples clearly show the advantages described of the method according to the invention.

Examples

30 Example 1:

A 40% by weight sodium sarcosinate solution with an analytically determined residual cyanide content of 930 ppm was heated up under pressure conditions (ca.
35 2.0 bar) to a temperature of 160°C. Test samples were withdrawn at fixed time intervals and the residual cyanide content was analyzed. The cyanide values obtained are recorded in table 1. The sodium sarcosinate content remains unchanged.

Table 1:

Time (min)	0	30	60	180
Cyanide content (ppm)	930	33	< 5	< 5

Example 2:

5

A 40% by weight solution of sodium sarcosinate with an analytically determined residual formaldehyde content of 900 ppm was heated up in the batch method under pressure conditions (ca. 2.0 bar) to 160°C and the decomposition of the formaldehyde was monitored in a time-dependent fashion in withdrawn test samples. The values obtained are recorded in table 2.

10

Table 2:

15

Time (min)	0	30	60	180
Formaldehyde content (ppm)	900	133	43	11

Example 3:

100 g of a 40% sodium sarcosinate solution with an analytically determined cyanide content of 760 ppm were treated, at room temperature, with the amount of 30% formaldehyde calculated according to formula 1.

20

Formula 1:

25

$$R_{FA} = \frac{C_{CN} * M_{SS} * MM_{FA} * 100}{MM_{CN} * Conc_{FA}}$$

$$R_{CN} = \frac{C_{FA} * M_{SS} * MM_{CN} * 100}{MM_{CN} * Conc_{CN}}$$

R = Requirement [g]

30

CN = Cyanide

FA = Formaldehyde

SS = Sarcosinate solution

M = Mass
MM = Molar mass [g/mol]
Conc. = Concentration [% by weight]
C = Content in the sarcosinate solution
5 [g/kg]

$$R_{FA} = \frac{0.76 * 0.1 * 31.0 * 100}{26.0 * 30} = 0.302 \text{ g}$$

10 This solution was heated to reflux under standard pressure (108°C) and was analytically investigated in a time-dependent fashion.

Table 3:

Time (min)	30	60
Cyanide content (ppm)	10	< 5
Formaldehyde content (ppm)	8	< 5

15

Example 4:

100 g of a 40% sodium sarcosinate solution with an analytically determined formaldehyde content of 929 ppm
20 were treated with the amount of cyanide (as NaCN solution; 15.9% by weight with regard to CN) calculated according to formula 1.

$$R_{CN} = \frac{0.929 * 0.1 * 26.0 * 100}{31.0 * 15.9} = 0.490 \text{ g}$$

25

The solution was, on the one hand, stirred at room temperature for 24 h (I) and, on the other hand, stirred at reflux temperature (108°C) in parallel (II), and analyzed.

Table 4:

	I	II	
Time/Temperature	24 h at RT	30 min at 108°C	60 min at 108°C
Cyanide content (ppm)	53	13	< 5
Formaldehyde content (ppm)	11	< 5	< 5